Rheological behaviour of $BaZrO_3$ suspensions in non-aqueous media

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Abstract

The colloidal behaviour of concentrated non-aqueous suspensions of barium zirconate is investigated. Optimum dispersing conditions are investigated for organic suspensions prepared with different solvent systems: methylethylketone (MEK)/ethanol, trichloroethylene (TCE)/ethanol, a methylisobutylketone (MIBK)/methylethylketone/cyclohexanone (CHN) and pure ethanol. Stabilisation of the suspensions is achieved by using two different dispersants: ester phosphate (EPH) and Hypermer KD-6. Rheological studies have been made in order to determine the optimum of each dispersant concentration as a function of the solvent systems. The best stabilisation of 30 vol.% suspensions is obtained by using EtOH with 3 wt.% KD-6 and TCE/EtOH with 1 wt.% EPH. Zeta potential studies show that the use of dispersants increases the positive surface potential on the particles. The zeta potential values increasing from +10 mV in the absence of EPH to +42 mV with 1.0 wt.% EPH and to +33 mV with KD-6. These results suggest that electrostatic repulsion plays an important role on the stability of these organic suspensions. Stabilised suspensions were slip cast in plaster molds and green densities higher than 55% of the theoretical density was obtained.

Keywords: Barium zirconate; Suspension; Rheology; Stabilisation; Organic solvents; Ceramics; Zeta potential

1. Introduction

Barium zirconate is a perovskite-type compound with a high melting point (2600 8C) and no high temperature phase transition. It can be used as a refractory material especially for the synthesis of superconductors. Barium zirconate is one of the best materials for manufacturing crucibles for the growth of $YBa_2Cu_3O_7$ superconducting single crystals. Pure $BaZrO_3$ substrate does not react with the highly corrosive phases present during the $YBa_2Cu_3O_7$ crystal growth process around 1000 8C.

Bulk ceramic parts like crucibles have been already used to test the efficiency of this material against corrosive materials [1,2]. Most of the $BaZrO_3$ parts produced have been made by pressing techniques [1,3]. Crucibles have recently been produced by a slip casting process using stable aqueous suspensions of barium zirconate dispersed with tetramethyl ammonium hydroxide (TMAH) and ammonium polymethacrylate (PMAA) [4,5].

It has been shown that barium zirconate is partially hydrolysed in water; barium ions are released into the suspension, thus modifying the stoichiometry (the Ba/Zr ratio) of the material. Barium zirconate parts must have a high chemical purity to be used in the synthesis of superconducting single crystals. The Ba/Zr ratio has to be strictly adjusted and controlled to avoid the formation of secondary phases at the grain boundaries. It has been proved that the presence of zirconia at the grain boundaries decreases the mean-life time of the crucibles and drastically modifies its corrosion behaviour [6]. It was demonstrated that barium content of the barium zirconate powder dispersed in water effectively decreases [4,5] thus to overcome the problem of barium release, a new investigation is proposed herein by using an organic solvent to produce stable suspensions.

In this study, barium zirconate suspensions are made with different organic solvents such as ethanol and the following azeotropic mixtures: methylethylketone (MEK)/ethanol, tri- chloroethylene (TCE)/ethanol, and methylisobutylketone (MIBK)/methylethylketone/cyclohexanone (CHN). Azeotro- pic mixtures are chosen to avoid the modification of solvent composition by evaporation. As defloculating agents a phosphate ester and an acrylic graft copolymer with polyethylene glycol (KD-6) were used. These organic surfactants are chosen on the basis of their efficiency for the stabilisation of $BaTiO_3$ suspensions in organic media. Some studies on the stability of $BaTiO_3$ in organic solvent can be found in the literature [7–9]. However, to the knowledge of the authors, no work has yet been done on the stabilisation of barium zirconate in such organic solvents.

Phosphate ester is one of the most popular surfactants used for the stabilisation of organic suspensions. Paik et al. [7] have studied the stabilisation mechanisms of $BaTiO_3$ particles using phosphate ester as a surfactant. They proved that the stabilisation is essentially the result of electrostatic repulsion between particles. This repulsion is created by a surface charge mechanism. These authors suggested that there is a competitive adsorption between EtOH and phosphate ester on $BaTiO_3$ surfaces. Negative charges of phosphate ester reduce the global charge on the particle.

Bhattacharjee et al. [8] were the first to stabilize a $BaTiO_3$ suspension in toluene–methanol using PVB. More recently, Tseng et al. [9] showed that PVB acts as a defloculating agent at low concentration and as a binder at higher concentration (2 wt.%) for $BaTiO_3$ suspensions in ethanol. High solid loading $BaTiO_3$ suspensions with low-viscosity can be obtained by adding acrylic graft copolymer to polyethylene glycol (KD-6) [10].

In this work, concentrated suspensions of barium zirconate (30 vol.%) were prepared in different dispersing media and the effect of EPH and KD-6 on the rheological behaviour was studied and compared. Suspensions were slip cast in plaster moulds in order to correlate the density of the green bodies with the dispersing conditions. The stabilisation mechanisms for the two selected deflocculants are discussed.

2. Experimental procedure

The barium zirconate used in this study (Alfa Aesar, 99% purity) was commercially available and produced by a solid- state reaction between $BaCO_3$ and ZrO_2. This powder has a specific surface area (BET) of 3.5 m^2/g and a particle size around 1.5 mm. For this study, the powder was milled in ethanol with zirconia balls in a planetary mill to reach a median particle size around 0.5 mm and a surface area (BET) of 10.6 m^2/g. Non-aqueous suspensions of $BaZrO_3$ were prepared up to a solid loading of 30 vol.% by mixing with an ultrasonic probe (IKA 400S, Germany) for 2 min, followed by 30 min low-speed mechanical agitation. As dispersing medium absolute ethanol (99.5% from Panreac, Spain), and the following azeotropic mixtures of solvents were tested: methylethylketone/ethanol (labelled as MEK/EtOH), trichloroethylene/ethanol (labelled as TCE/EtOH), and methylethylketone/methylisobutylketone/ cyclohexanone (labelled as MEK/MIBK/CHN). The first two mixtures are widely used in tape casting technology for ceramic suspensions, while the last one was successfully used in tape casting of non-aqueous silicon nitride slips [11]. Table 1 gives the main physical and chemical properties of these solvents.

A phosphate ester (Emphos PS21A, Whitco Chem., USA, labelled as EPH), and an acrylic graft copolymer added to polyethylene glycol (Uniqema, ICI group, labelled as KD-6) were used as deflocculating agents. Concentrations are expressed as weight % (wt.%), referred to dry solids.

The colloidal behaviour was studied through zeta potential determinations by using Zetasizer Nano-ZS (Malvern, UK) equipment, which uses the laser Doppler principle combined with non-invasive back-scattering (NIBS). This instrument is suitable for measuring the zeta potential of particles with mean sizes ranging from 1 nm to near 10 mm, although previous calibration is required to select optimum measuring conditions. Suspensions were prepared in ethanol and diluted to 10^{-2} g/l for the measurements.

The rheological behaviour of all studied slips was determined using a rheometer (Haake RS50, Thermo Electron, Germany) operating at both controlled shear rate (CR) and controlled shear stress (CS) conditions. The controlled shear rate was used to measure the flow curves with a three-stage measuring program with a linear increase of shear rate from 0 to 1000 s^{-1} in 180 s, a plateau at 1000 s^{-1} for 60 s and a decrease to zero shear rate in 180 s. The thixotropy was measured by the hysteresis area enclosed between the up-curve and the down-curve in the controlled rate flow curves. The controlled shear stress was used for determining the apparent yield values, calculated from the double logarithmic plots of deformation versus shear stress [12]. The measurements were performed using a double cone and plate system, with a solvent trap, at a constant temperature of 25 8C.

The studied suspensions were slip cast on plaster of Paris moulds to obtain discs with 2 cm in diameter in order to establish the proper relationships between processing variables and green body density. The density of the green bodies was measured by mercury immersion after drying for 48 h at room conditions and the values are reported as % of theoretical density of $BaZrO_3$ (6.23 g cm^{-3}).

Table 1: Physical and chemical properties of organic solvents

Solvent	Acidity	Viscosity at 20 8C (mPa s)	Dielectric constant	A_L (10^{-20} J) Hamaker constant
EtOH	Acid	1.2	24	6.37
TCE	Acid	5.5	3.0	5.91
MEK	Basic	0.4	15.45	5.17
MIBK	Basic	0.8	13.11	5.33
CHN	Basic	1.1	18.3	7.39

3. Results

3.1. Study of the $BaZrO_3$ dispersion using EPH

In order to study the effect of organic solvents on the rheological properties of $BaZrO_3$ concentrated slips (30 vol.%), all suspensions were first prepared with a constant concentra- tion of phosphate ester (EPH) equal to 0.6 wt.%. This surfactant (EPH) has already been used with success to stabilize $BaTiO_3$ concentrated suspensions [7,13,14]. Fig. 1 shows the flow curves of the slips containing 0.6 wt.% EPH for different solvent systems measured in controlled rate mode. The slip prepared with the mixture MEK/MIBK/CHN was very viscous and had significant thixotropy, while the other slips had low- viscosity and no thixotropy. The lowest viscosity was found for the solvent MEK/EtOH in the high shear region. However, in this figure a magnification of the low-shear region of the flow curves (corresponding to the shearing range by the blades in tape casting which occurs, normally below 50 s^{-1}) is also plotted for the three low-viscosity slips (excluding that prepared with MEK/MIBK/CHN). This plot shows that the slip prepared with TCE/EtOH had the lowest viscosity and nearly Newtonian behaviour, while that prepared with MEK/ EtOH had the highest viscosity and shear-thinning behaviour. The fit for this curve was obtained with the Herschel–Bulkley model, while the slip with EtOH has been fitted with the Casson model. It must be noted that EtOH slurry shows a larger thixotropy than TCE/EtOH and MEK/EtOH slurries. This behaviour could be attributed to the formation of hydrogen bondings between particles and solvent in pure ethanol slurry. In the case of the solvent mixtures less ethanol is present to make hydrogen bondings.

The main rheological properties of these suspensions are summarized in Table 2. The last column in this table shows the green density values of ceramic parts produced by a slip casting process. These results confirm the stability of the suspensions through the reported green density values. Maximum green density of 57.7% TD is obtained for the slip prepared with the TCE/ETOH solvent, which is the most stable suspension.

From the above results, the suspensions based on pure EtOH and on TCE/EtOH seem to have the best rheological behaviour. Thus, these suspensions were selected for further optimisation with EPH as deflocculant.

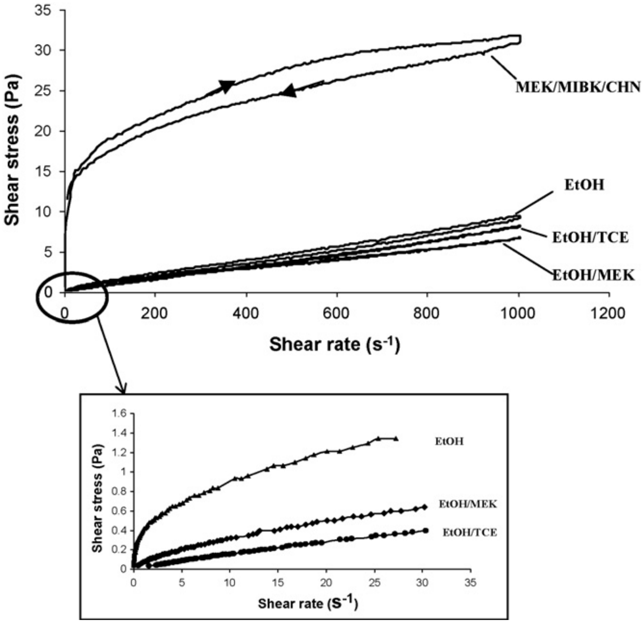

Fig. 1. Flow curves of suspensions with 30 vol.% solids prepared with different solvents. In the bottom, a magnification of the low-viscosity and low-shear region is shown.

Table 2 : Rheological parameters of 30 vol.% slips of $BaZrO_3$ in different solvents dispersed with 0.6 wt.% EPH and relative density of green casts

Solvents (wt.%)	Yield stress (Pa)	Thixotropy (Pa/s)	Viscosity at 100 s^{-1} (mPa s)	Green density (%)
EtOH (100)	0.3	520	15	52.4
EtOH/TCE (27/73)	0.0	180	9	57.7
EtOH/MEK (40/60)	0.0	250	12	55.6
MEK/MIBK/CHN (36.7/29.8/33.5)	7.5	2500	196	47.4

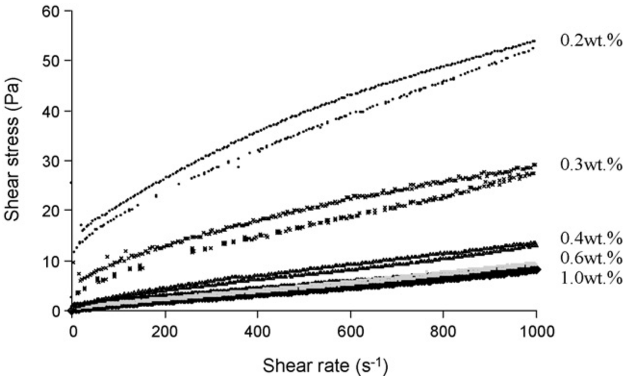

Fig. 2. Flow curves of 30 vol.% slips prepared in EtOH with EPH as deflocculant.

Fig. 2 shows the CR-flow curves of slips made in pure ethanol with different concentrations (wt.%) of EPH. Better dispersion is reached with EPH contents of 0.4–1.0 wt.%, but lower EPH contents led to high viscosity and some thixotropy. Similar results were obtained for suspensions prepared in TCE/ ETOH, so the corresponding flow curves are not shown.

The variation of viscosity with EPH concentration for slips prepared with EtOH and TCE/EtOH is plotted in Fig. 3. The viscosity of suspensions prepared in TCE/EtOH is lower than that in EtOH for any concentration of EPH. Minimum viscosity is reached for 0.6 wt.% of EPH in pure EtOH and for 1 wt.% EPH for TCE/ETOH. Tables 3 and 4 report the rheological parameters of slips made with pure EtOH and TCE/EtOH, respectively. The resulting relative density of green bodies obtained by slip casting is shown in the last column of Tables 3 and 4, also. The maximum green density is around 54%TD for 1 wt.% EPH in EtOH, while suspensions in TCE/EtOH led to relative densities >57.5% of TD for concentrations of EPH of 0.4–1.0 wt.%. Suspensions with MEK/MIBK/CHN were not optimized in this study but qualitative tests showed that around 3 wt.% EPH was necessary to obtain a fluid suspension.

The yield stress was measured at the intercepting point of the two straight lines drawn in the log-log plot of strain versus shear stress measured in controlled stress mode. As an example, Fig. 4 shows the log–log plot of shear stress versus deformation of suspensions prepared in EtOH and different EPH contents. This figure shows that the systems containing more than 0.3 wt.% EPH are not plastic and then present no yield stress. Colloidal stability of $BaZrO_3$ non-aqueous suspensions was also studied in terms of zeta potential. Fig. 5 shows the evolution of zeta potential of the barium zirconate particles dispersed in pure EtOH as a function of the EPH concentration. It can be seen that barium zirconate particles in EtOH are characterized by a positively charged surface, with a zeta potential of +10 mV due to the interaction with the solvent. A maximum zeta potential of +42 mV is reached for an EPH concentration of 1.0 wt.%.

3.2. Study of the BaZrO3 dispersion using KD-6 Hypermer

KD-6 is a non-ionic surfactant containing acrylic graft copolymer with polyethylene glycol. Thus, it could be used to avoid the contamination of the sintered ceramic parts by phosphate ions. Acrylates and, in particular, polymethacrylate surfactants have been already used with success in the deflocculation of $BaTiO_3$ and $BaZrO_3$ aqueous suspensions with high solid loading [4,5,10,15–17]. However, polymetha- crylate salts are not soluble in organic solvents so they cannot be used to stabilise $BaZrO_3$ organic suspensions. Therefore, Hypermer KD-6 seem to be a good alternative to classical polymethacrylate surfactant for stabilizing non-aqueous suspensions. Tseng et al. [9,10,18] have used KD-6 surfactant successfully for stabilizing barium titanate and nickel slurries dispersed in alcohol with high solid loading.

As in the previous case, $BaZrO_3$ slips were prepared to a concentration of 30 vol.% in the following solvents systems: EtOH, TCE/EtOH and MEK/MIBK/CHN. The suitable KD-6 concentration was previously estimated by qualitative tests to be around 3 wt.%.

Fig. 6 shows the CR-flow curves of the slips containing 3.0 wt.% KD-6 for the different solvent systems measured in controlled rate. The main rheological properties of these suspensions are summarized in Table 5. Slips formed with EtOH and TCE/EtOH show a nearly Newtonian behaviour. The MEK/MIBK/CHN suspension shows a very shear-thinning behaviour with a large thixotropic loop. This slip shows the maximum viscosity and thixotropy, the viscosity being over 10 times more than that obtained with pure EtOH as solvent. Suspensions prepared in EtOH have the lowest viscosity (around 9 mPa s for a shear rate of 100 s^{-1}) and no apparent yield stress can be obtained by the log–log intersection method. A maximum green density of around 58.5% TD is obtained by slip casting. Thus, EtOH was selected as the best solvent for suspensions dispersed with KD-6.

Fig. 7 shows the flow curves of suspensions prepared in EtOH with different KD-6 concentrations. The main rheolo- gical properties of these slips are summarized in Table 6. A minimum viscosity is reached by addition of 3.0 wt.% KD-6, although an excess of KD-6 seems to have no significant effect on the rheological parameters of the slip (Table 6). The suspensions containing 1.5 wt.% KD-6 are characterised by a false shear-thickening, time-dependent behaviour. Slips con- taining between 2.5 and 4 wt.% KD-6 show a low-viscosity and no thixotropy. Ceramic parts manufactured by slip casting show a green density around 58% TD.

The surface behaviour was investigated by zeta potential measurements. Fig. 8 shows the evolution of the zeta potential of $BaZrO_3$ suspensions in EtOH as a function of KD-6 concentration. The zeta potential of the particles in pure ethanol without Hypermer is around +10 mV and a maximum around+33 mV is reached for a KD-6 concentration of 3 wt.%.

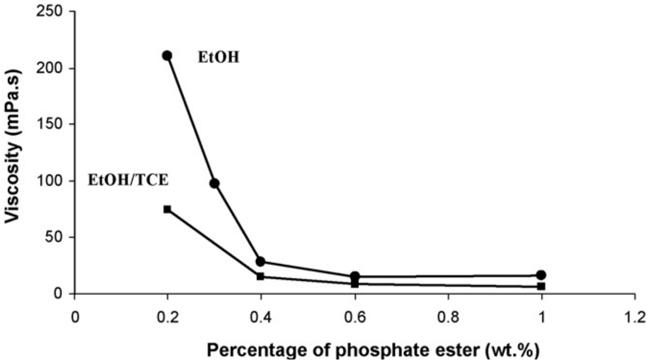

Fig. 3. Variation of viscosity of 30 vol.% slips prepared in EtOH and TCE/ EtOH with EPH content.

Table 3: Rheological parameters of 30 vol.% slips of BaZrO3 in EtOH for different EPH contents and relative density of green casts

EPH (wt.%)	Yield stress (Pa)	Thixotropy (Pa/s)	Viscosity at 100 s^{-1} (mPa s)	Green density (%)
0.2	15.5	3000	211	–
0.3	7.5	4350	97	48.6
0.4	No	1080	28	51.7
0.6	No	520	15	52.4
1.0	No	700	17	54.0

Table 4: Rheological parameters of 30 vol.% slips of BaZrO3 in TCE/EtOH for different EPH contents and relative density of green casts

EPH (wt.%)	Yield stress (Pa)	Thixotropy (Pa/s)	Viscosity at 100 s^{-1} (mPa s)	Green density (%)
0.2	2.8	1160	54.3	–
0.4	No	143	15.5	57.5
0.6	No	180	9	57.7
1.0	No	127	6.8	57.6

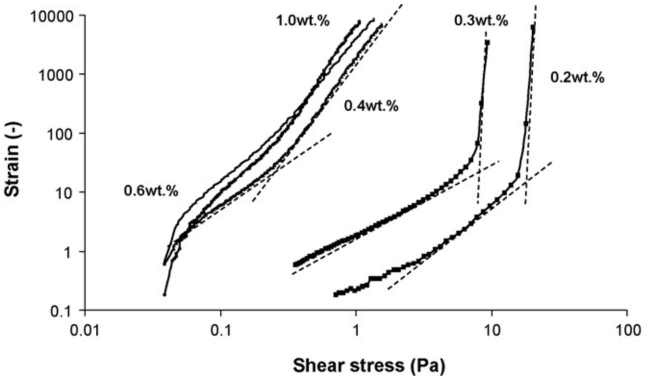

Fig. 4. Log–log plot of deformation versus stress for EtOH suspensions with different contents of EPH.

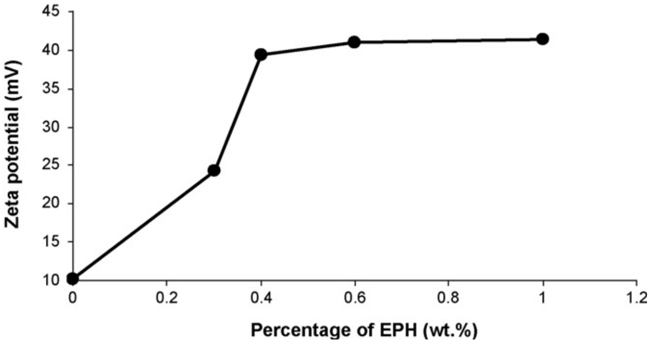

Fig. 5. Evolution of zeta potential of barium zirconate suspensions in EtOH as a function of EPH content.

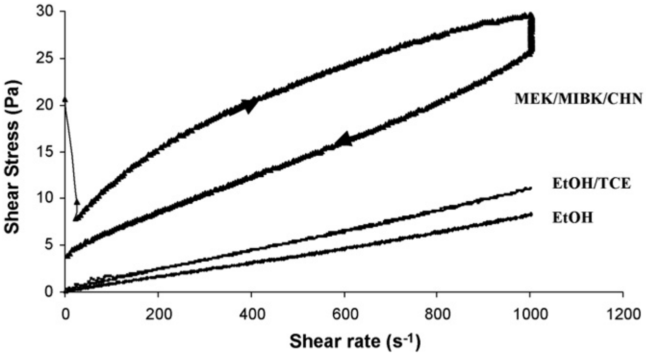

Fig. 6. CR-flow curves of 30 vol.% slips containing 3.0 wt.% KD-6 in different solvents.

Table 5 : Rheological parameters of 30 vol.% slips of BaZrO3 in different solvents dispersed with 3.0 wt.% KD-6 and relative density of green casts

Solvents	Yield stress (Pa)	Thixotropy (Pa/s)	Viscosity at 100 s^{-1} (mPa s)	Green density (%)
EtOH	No	170	8.9	58.5
EtOH/TCE	No	241	13	57.2
MEK/MIBK/CHN	–	7450	116	43.5

Table 6: Rheological parameters of 30 vol.% slips of BaZrO3 in EtOH for different KD-6 contents and relative density of green casts

KD6 (wt.%)	Yield stress (Pa)	Thixotropy (Pa/s)	Viscosity at 100 s^{-1} (mPa s)	Green density (%)
1.5	1, 2	1140	26.7	50.6
2	No	442	13.5	55.5
2.5	No	18	11	58.1
3	No	170	8.9	58.5
4	No	100	10.9	58.3

4. Discussion

4.1. Dispersion using EPH

The presence of EtOH as dispersing medium seems to contribute to the dispersion of barium zirconate using EPH (Figs. 1 and 2). The rheological parameters of the slips containing EtOH confirm the effective role of EtOH in the deflocculation mechanism. To explain it, it is important to remind that EtOH is an acidic organic solvent (Table 1) and barium zirconate powder has a basic surface. Thus, proton exchange between the acidic solvent and the basic particle surfaces would be effective. MEK, MIBK and CHN are basic organic solvents and no proton exchange is expected to occur between the powder surface and the solvents. Consequently, the suspension made in MEK/MIBK/CHN with EPH is highly flocculated as a result of the low surface charge. However, suspensions with low concentration of EPH (0.2 wt.%) show a high viscosity even in the presence of EtOH (Tables 3 and 4). The optimum slip stability is reached for an addition of 0.6 wt.% EPH. Both EtOH and EPH play a crucial role in the charging mechanism for the stabilisation of barium zirconate particles.

Paik et al. [7] studied $BaTiO_3$ suspensions dispersed in EtOH with EPH, showing that there is a competitive adsorption between EPH and EtOH, which developed an opposite surface charge on the $BaTiO_3$ particles. So, addition of EPH to the slurry can cause the reduction of the total positive surface charge by adsorption of phosphate anions on the positive surface charges. Thus, the contribution of electrostatic forces to the suspension stability should be lowered. However, the results obtained in the present work (Fig. 5) seem to demonstrate that the addition of EPH even in low quantity increases the positive surface charge of barium zirconate particles, the zeta potential values increasing from +10 mV in the absence of EPH to by +42 mV with 1.0 wt.% EPH. These results are in good agreement with those obtained by rheological measurements (Fig. 3). These results suggest that electrostatic repulsion has an important role on the stability of the suspension in good agreement with the conclusions of Cannon et al. on the stabilization of $BaTiO_3$ suspensions with EPH in MEK/ethanol [13]. Positive surface charge could be explained by the model of charging particles in solvents proposed by Fowkes et al. [19]. Surfactants molecules (EPH) come to the basic sites of the particles surface and they are ionized before leaving them and giving protons on the particle surface.

However, in MEK/MIBK/CHN suspension, no proton exchange between particle surface and basic solvents can take place. Lee and Paik [20] have shown that the adsorption of an acidic surfactant on basic alumina surface depends on the acidity of the solvent. The adsorption decreases with the acidity of the solvent. Hence, for a basic solvent larger amount of surfactant can be adsorbed on the particle surface. This can explain the larger concentration of EPH (3 wt.%) necessary to stabilise the suspension in MEK/MIBK/CHN. So, a more compact layer of EPH is adsorbed on particles in MEK/MIBK/ CHN system which leads to the formation of a steric barrier. Recently, Gutierrez and Moreno [11] have shown that EPH can be used with success to stabilize concentrated silicon nitride slurries made with MEK/MIBK/CHN. They proved by calculation that EPH can stabilise the slurry by steric repulsion at short separation distances but electrostatic forces are acting at greater separation distances.

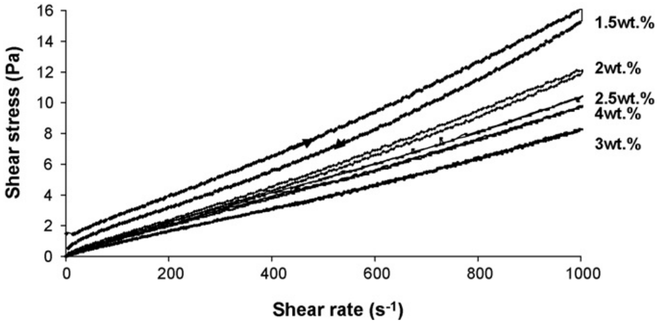

Fig. 7. Flow curves of 30 vol.% slips prepared in EtOH with different KD-6 concentrations.

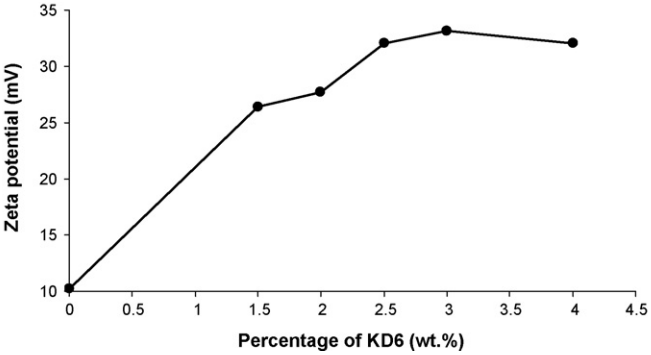

Fig. 8. Evolution of zeta potential of barium zirconate suspensions in EtOH as a function of KD-6 content.

4.2. Dispersion using KD-6 Hypermer

The best solvent to prepare stable barium zirconate suspensions with KD-6 seems to be ethanol. Solvents containing ethanol (EtOH and TCE/EtOH) are more effective than those without EtOH, like MEK/MIBK/CHN. However, when using KD-6 as deflocculating agent, the addition of TCE to EtOH does not improve the stability of the suspension but increases the thixotropy. TCE/EtOH mixture has a lower dielectric constant than pure EtOH. Thus dielectric constant of the solvent has to play a role in the stabilisation mechanism. The suspensions containing KD-6 surfactant are quite different than those prepared with EPH as deflocculating agent. Suspensions with KD-6 have lower viscosity and thixotropy (i.e. weaker structures are formed), thus suggesting that hydrogen bonding between particles and solvent is less favoured.

To explain the different behaviour of slips containing KD-6 or EPH, it is necessary to consider the surface charge of the barium zirconate particles. The zeta potential increases up to +33 mV when adding 3 wt.% KD-6. The suspension containing only 1.5 wt.% KD-6 has a zeta potential around +26 mV. This suspension shows a viscosity three times higher than that containing 3.0 wt.% KD-6. The small difference in the zeta potential does not explain the large difference of stability. Hence, it must be expected that the increased stability of the suspension when the KD-6 concentration decreases, should be related to an important steric contribution that cannot be quantified by zeta potential measurements. In fact, suspensions stabilised with KD-6 exhibit higher stability (lower viscosity and higher green densities) than those stabilised with EPH, although the latter gives higher zeta potentials (up to +42 mV). Although a proton exchange mechanism could occur for both deflocculants, their different affinity for EtOH determines the charging mechanism. EPH molecules are charged and smaller than KD-6 ones. Thus, solvatation would be easier to occur for EPH molecules than for KD-6 molecules. KD-6 are copolymer molecules characterised by acrylic groups grafted on a long hydrocarbon chain. The polarity of the molecule is due to the acrylic groups fixed to the molecule. Then, KD-6 molecules, having lower affinity with the solvent, can be easily attached to the particle, so that the negative charges of KD-6 chains will lower the global surface charge of the particles (+33 mV instead of +42 mV). Solvatation of KD-6 molecules is favoured in a solvent with a higher dielectric constant, that is why it is better to use EtOH than TCE/EtOH. Then, chains absorbed onto the particles surfaces are more extended toward the liquid and steric repulsion becomes more important.

5. Conclusions

Concentrated non-aqueous suspensions of barium zirconate can be stabilised using EPH and KD-6. In the presence of an acidic solvent, and particularly ethanol, the electrostatic contribution to the total stabilisation is very important for both defloculants. The proton exchange between the surfactant molecules and the barium zirconate surface could explain the positive surface charge of the particles in ethanol. The suspensions stabilised with 0.6 wt.% EPH show the better rheological parameters for suspensions made with TCE/ETOH. The use of TCE reduces hydrogen bondings and allows to obtain suspensions with lower viscosity and thixotropy. 30 vol.% $BaZrO_3$ suspensions were cast and ceramic parts with a maximum green density of 57% of TD were manufactured.

When using KD-6 as defloculant, EtOH is the best solvent. The thixotropy of the suspension (30 vol.%) is very low, which proves that hydrogen bondings are not very important even in pure EtOH. The affinity between the KD-6 molecules and the organic solvent is lower than for EPH. Thus, KD-6 molecules can be more adsorbed onto the particle surface causing a reduction of the total positive charge in comparison with EPH. However, suspensions stabilised with KD-6 show a better stability than slips containing EPH. This behaviour could be explained by a more efficient steric stabilisation due to the length of the KD-6 copolymer molecules. 3 wt.% KD-6 allow to reach the better rheological parameters for a concentrated barium zirconate suspension (30 vol.%) in pure EtOH. 30 vol.% $BaZrO_3$ suspensions were cast and ceramic parts with a maximum green density of 58.5%TD were manufac- tured.

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